

of the $\text{Fe}(\text{CN})_6^{3-}$ reduction increasing ca 4 times on substituting Cs^+ to K^+) as well as the value of the temperature coefficient point to a great importance of the interaction between the anion and the next neighbouring cation in the double layer. It is possible that in the case of the tervalent ferricyanide anion the simultaneous interaction with two or three neighbouring cations has to be taken into account. As these interactions have not been considered while deducing eq.(5) ^{and (6)} these can give only roughly approximate results.

I have tried to show that the close connection between the adsorption of ions and their participation in electrode processes can be demonstrated with the help of many independent methods. I think that the results obtained may help to solve similar problems in other branches of electrochemical kinetics, where the role of the adsorption of the reacting substance has not been sufficiently elucidated up to now, as for instance in the case of the irreversible reduction of many organic compounds.

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Subscripts to figures.

Fig.1. Dependence of the shift of the potential $\Delta\phi$ on the initial concentration of the ion adsorbed c.

1. KCl,					
2. KBr,	∞	∞	∞	∞	
3. KJ,	∞	∞	∞	∞	
4. KBr,	∞	∞	∞	∞	0,3 v.

Platinized Pt-electrode. Potentials referred to hydrogen electrode in n H_2SO_4 .

Fig.2. Electrocapillary curves of mercury in n KNO_3 + 0,01 n HNO_3 + x $TlNO_3$. ϕ vs N.C.E.
Curves from top to bottom: x=0; 0,01 n; 0,1 M; 0,2 n.

Fig.3. Effect of Cd^{2+} ions adsorption on the anodic charging curves of platinized Pt.
Charging curves: 1 - in n H_2SO_4 ; 2 - in n H_2SO_4 + 0,1 n $CdSO_4$; 3 - in n H_2SO_4 after adsorption of Cd^{2+} from n H_2SO_4 + 0,1 n $CdSO_4$ (initial potential 0,3 v) and a repeated washing of the electrode with n H_2SO_4 ~~(that restored the initial form of the curve)~~; 4 - in n H_2SO_4 after the cleaned electrode has been kept in this solution for 80 hours. Curve 4 shows that some Cd reappears on the surface, diffusing back from deeper layers. The curves 3 and 4 are shifted along the abscissae axis by 0,2 v.
 ϕ referred to hydrogen electrode in n H_2SO_4 .

Fig.4. Dependence of the charge density of mercury ϵ on overvoltage η .

1 - n HCl + 2 n HCl;
2 - n HCl + 2 n KBr;
3 - n HCl + 2 n KJ.

Fig.5. Dependence of the overvoltage η on the log of the current density i .
 1 - n HCl + 2 n KCl ;
 2 - n HCl + 2 n KBr ;
 3 - n HCl + 2 n KJ.
 Dotted curves calculated according to eq.(3).

Fig.6. Dependence of the coverage of a growing mercury drop with the adsorbed layer θ on the concentration c of $N(C_4H_9)_4J$ (in the presence of n KJ).
 1 - $\varphi = -1,0$ v ; 2 - $\varphi = -1,3$ v ;
 3 - $\varphi = -1,4$ v ; 4 - $\varphi = -1,47$ v ;
 5 - $\varphi = -1,5$ v ; 6 - $\varphi = -1,53$.
 Dotted curve calculated according to the equation of Ilcovič. φ vs. N.C.E.

Fig.7. Electrocapillary curves of mercury.
 1 - 0,1 n $N(C_3H_7)_4Cl$;
 2 - 0,1 n $N(C_3H_7)_4J$.

Fig.8. Dependence of the differential capacity C on the potential in the neighborhood of the desorption potential.
 1 - n KCl + 10^{-3} n $[N(C_4H_9)_4]_2 SO_4$;
 2 - n KBr + 10^{-3} n $[N(C_4H_9)_4]_2 SO_4$;
 3 - n KJ + 10^{-3} n $[N(C_4H_9)_4]_2 SO_4$.
 A.C.frequency 1000 Hz.

Fig.9. Dependence of the overvoltage on the log of the current density. Dropping mercury electrode.
 1 - 2 n HCl + 2 n KCl ;
 2 - 2 n HCl + 2 n KJ ;
 3 - 2 n HCl + 2 n KCl + $4,5 \cdot 10^{-4}$ n $N(C_4H_9)_4 Br$;
 4 - 2 n HCl + 2 n KJ + $4,5 \cdot 10^{-4}$ n $N(C_4H_9)_4 Br$;

Fig.10. Dependence of the rate of the electroreduction of $\text{Fe}(\text{CN})_6^{3-}$ on the potential (vs.N.C.E.). The rate, ~~am~~ given per cm^2 .

- 1 - 10^{-3} n $\text{K}_3\text{Fe}(\text{CN})_6$;
- 2 - 10^{-3} n $\text{K}_3\text{Fe}(\text{CN})_6$ + $0,5 \cdot 10^{-3}$ n KCl ;
- 3 - 10^{-3} n $\text{K}_3\text{Fe}(\text{CN})_6$ + 10^{-3} n KCl ;
- 4 - 10^{-3} n $\text{K}_3\text{Fe}(\text{CN})_6$ + $1,5 \cdot 10^{-3}$ n KCl .

Fig.11. Dependence of the rate of the electroreduction on the potential (vs.N.C.E.).

- 1 - 10^{-3} n $\text{Li}_3\text{Fe}(\text{CN})_6$;
- 2 - 10^{-3} n $\text{Li}_3\text{Fe}(\text{CN})_6$ + $2 \cdot 10^{-3}$ n LiCl ;
- 3 - 10^{-3} n $\text{Li}_3\text{Fe}(\text{CN})_6$ + $3 \cdot 10^{-3}$ n LiCl .

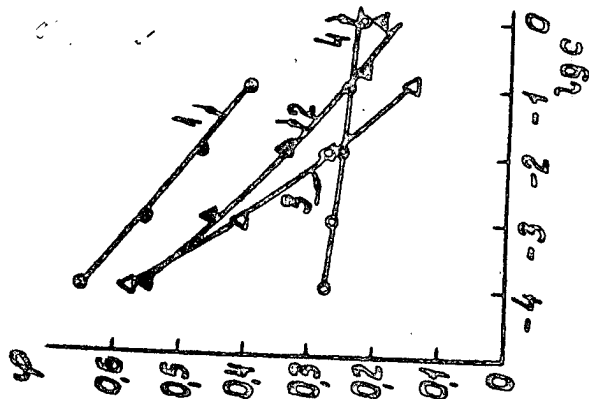


Fig. 1

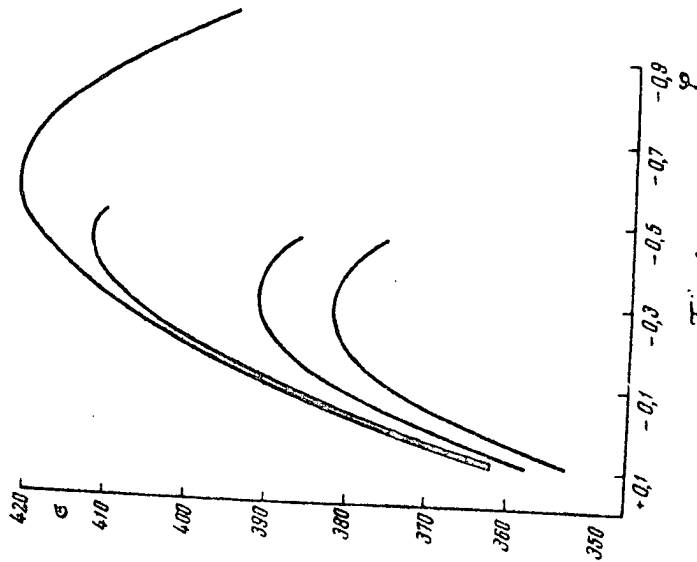


Fig. 2

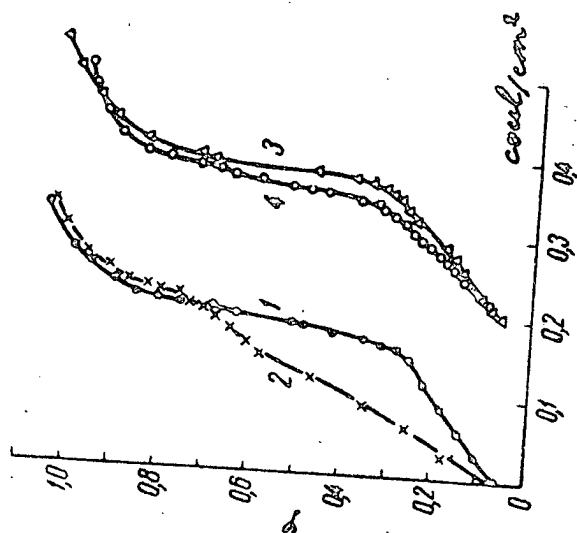


Fig. 3

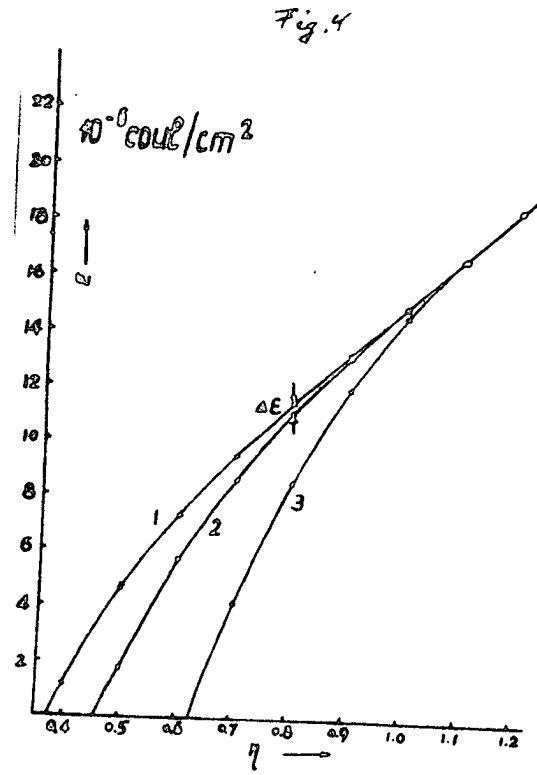


Fig. 4

Fig. 5

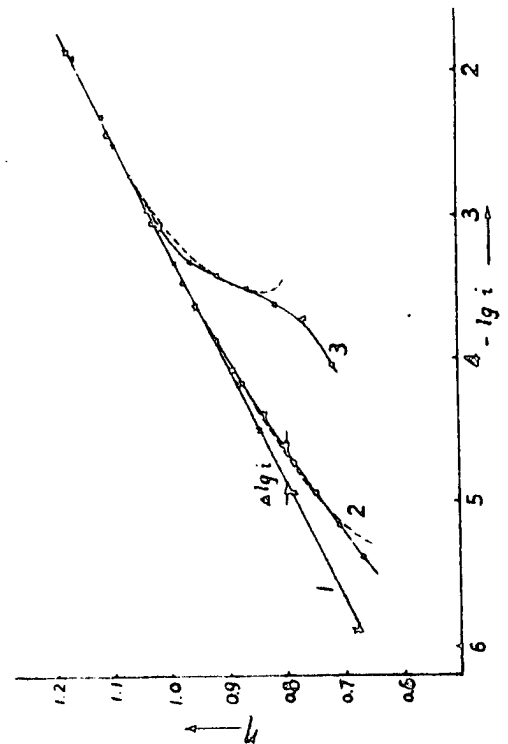


Fig. 6

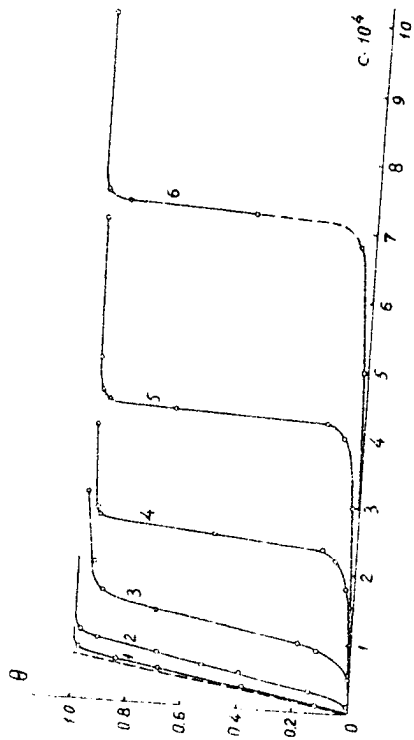


Fig. 7

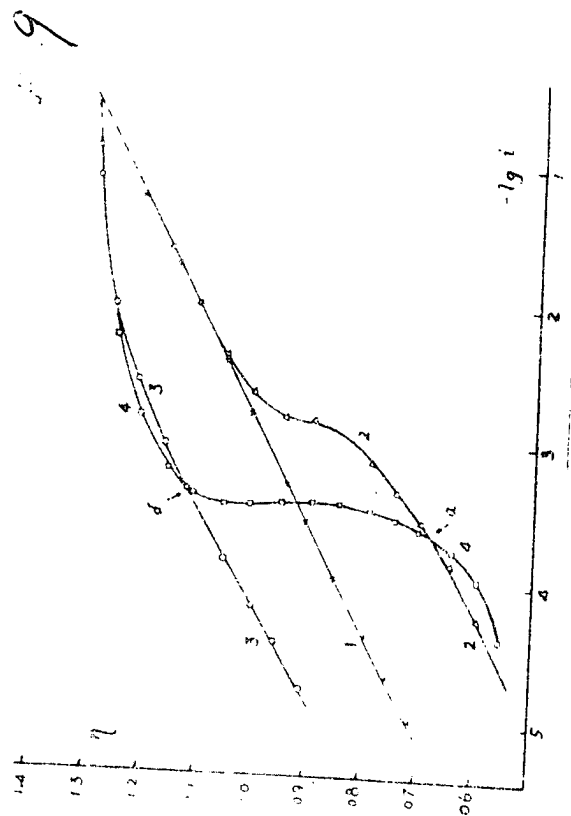
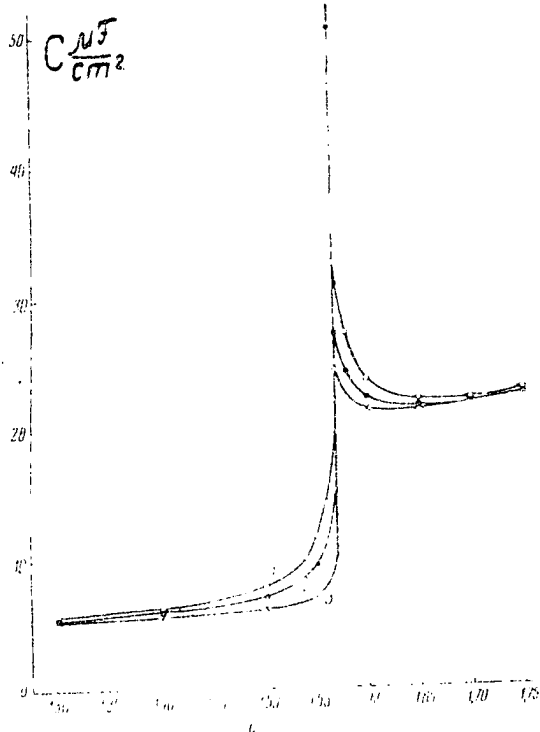
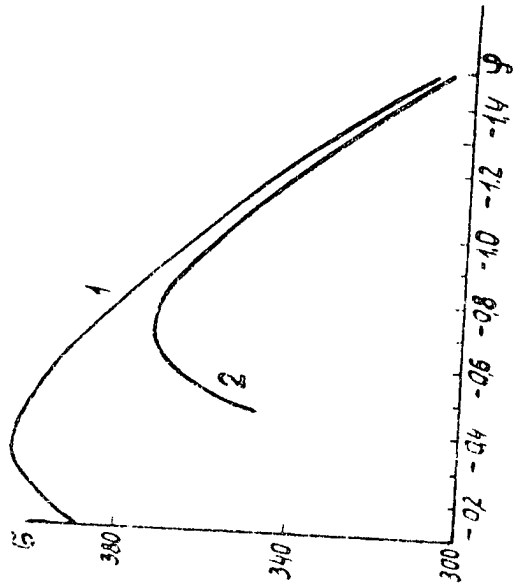


Fig. 10

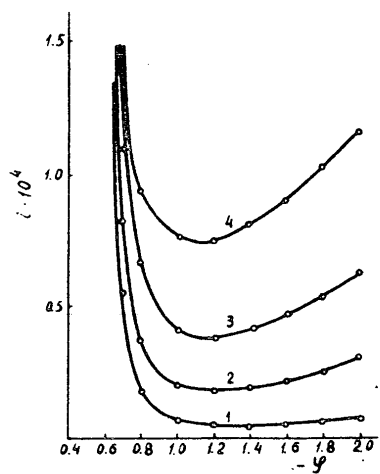
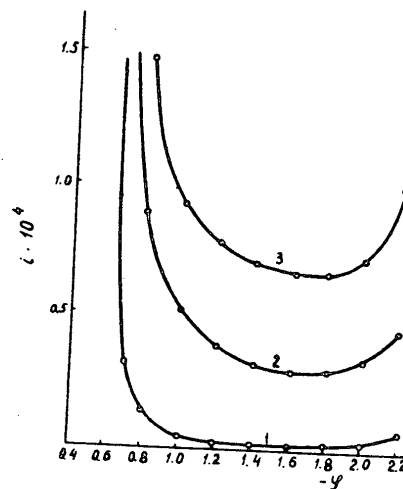


Fig. 11



EFFECT OF SPECIFIC ADSORPTION OF ANIONS ON
THE KINETICS OF ANODIC DISSOLUTION OF SOME METALS

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J.M. Kolotyrkin, Moscow.

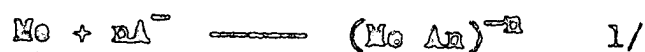
The dissolution rate of some metals in solutions of electrolytes depends greatly not only on PH, but also on the anion composition of the solution. This influence of the anions is often connected with their action on the state of the passivating layer, i.e. on the diffusion barrier. In recent years data has been obtained pointing to the direct participation of the electrolyte anions in the reactions of the discharge and the formation of metallic ions. Such data was obtained in the works of Heyrovsky¹⁾, Randles²⁾, Gerisher³⁾, Pionteli⁴⁾ and the author of this paper.

In investigations carried out by the author together with L.A. Medvedeva⁵⁾ on the influence of haloid salts on the rate of dissolution of cadmium in acid solutions, it was established that the overvoltage of the anodic process in this case depends greatly on the nature and concentration of the salts. The overvoltage begins to decrease noticeably from a certain concentration of the salts; the concentration becomes less as the adsorbability of the haloid ion grows, i.e. it decreases with the transition from Cl to Br and I.

In explaining these results it was assumed that

-2-

the activating influence of the anions on the process of anodic dissolution is connected with the specific adsorption of these anions on the surface of the electrode. Evidently such adsorption can under certain conditions bring about a noticeable decrease of the potential barrier which the metal ion must overcome on transition from the metal phase into the solution. Physically it probably means that the replacement of molecules of water by specifically adsorbed anions at the surface of the dissolving metal is in this case accompanied by an increase in the overlaying of the energy fields which act on the ion from the metallic lattice and the solution. Under these circumstances, the surface atom of the metal is included in the electronic atmosphere of the anion, which inevitably leads to a weakening of its ties with neighbouring atoms and facilitates the transition from the metallic phase into the solution in the form of a complex compound with adsorbed anions. The mechanism of the dissolution of the metal in this case can be represented in the form of the following two consecutive reactions:



The first of these reactions correspond to the specific

-3-

adsorption of the anion on the surface of the metal with the formation of a complex and the second --with the ionisation of the compound that follows. The kinetics of this process can be expressed by the following equation:

$$i_a = K, C_g^{\delta} \exp\left(\beta \frac{F}{RT} \varphi\right) \quad 3/$$

where C_g is the concentration of the haloid salt.

Similar results were obtained recently in another experiment carried out in our laboratory by V.V. Losev⁶⁾, who investigated the effect of anions on the process of anodic dissolution of Indium amalgam. Radioactive indicators were used and with their help the exchange currents between the amalgam and solutions of Indium salt were measured at corresponding equilibrium potentials. By combining this method with the usual polarisation measurements it was also possible to investigate the kinetics of the anodic reaction.

Measurements were carried out in a cell shown on figure I. In the upper part of the cell a radioactive amalgam of Indium was prepared by electrolysis of the corresponding solution. It was then poured into the main, lower part of the cell and a solution of Indium salt was introduced from an adjacent auxiliary cell. Preparation of the amalgam and all measurements were

-4-

conducted in an atmosphere of nitrogen free of oxygen. The amalgam and solution were vigorously stirred by a magnetic stirrer. The experiments were conducted at a constant concentration of Indium in the amalgam and the solution; a constant ionic strength of the solution (3M) was maintained by adding NaClO_4 .

After the amalgam came into contact with the solution it was polarised cathodically. At the same time together with the cathodic process of discharge of Indium ions, the process of ionisation of the atoms of Indium takes place as well, although at a slower rate. The increase of radioactivity of the solution was a measure of the rate of the anodic reaction ^{x)}.

With the help of this method the influence of the concentration of the Sodium haloid salts on the rate of dissolution of 0,1M amalgam of Indium in solutions of 0,01M NaClO_4 + 0,001M HClO_4 was measured at different potentials and in particular at equilibrium potential (exchange current).

The results of measurements showed that the dependence of the rate of the true anodic process on the potential is characterised in this case by a Tafel line with a slope of 0,025 V. One of these lines is given

x) A more detailed explanation of the method is given in 7/.

-5-

on figure 2. The current polarisation curve received in this experiment is also plotted on figure 2. Figure 2 shows that given a sufficient shift from the equilibrium potential in the positive direction the true anodic curve received by radiochemical methods coincides with the anodic current polarisation curves.

It should be pointed out that the slope of the Tafel line and consequently the transition coefficient $\beta = 2,3 \frac{RT}{\beta_a F} = 2,32$ remain constant although the nature of the haloid salt and its concentration in the solution changed. The introduction of haloid salts, however, brings about a noticeable decrease in the overvoltage of the anodic process. One can see this on figure 3, where the curve characterising the dependence of dissolution rate of Indium amalgam at constant potential on the concentration of NaCl is plotted. A similar dependence was received also for NaBr and NaI (figure 4).

As can be seen from the abovementioned data, beginning from a certain concentration, which increases on transition from I^- to Br^- and Cl^- , the subsequent concentration increase of the haloid salt in the solution brings about an increase in the dissolution rate of Indium amalgam. Judging from the slope of the upper section of the curves on figure 3 & 4, the order of the anodic reaction by the haloid ions changes noticeably on transition from Cl^- to Br^- and I^- . Thus, for instance, if

-5-

in the presence of NaCl (when $C_g > 0,50$ n.) the kinetics of the electrode reaction can be expressed by equation /3/ with coefficient " δ " almost equal to 3, then in the presence of bromides (when $C_g > 0,05$ n.) and iodides (when $C_g > 2 \cdot 10^{-3}$ n.) this coefficient must be taken to be 2 and 1 correspondingly.

To understand the mechanism of the anions' influence on the kinetics of the electrode reaction it is necessary to examine the behaviour of current exchange (i_0) for Indium amalgam under the same conditions. As shown by V.V. Lenev, the increase of the concentration of NaCl to 0,5 M does not bring about an increase in the exchange current, which, as in the initial solution, remains equal to $1,6 \cdot 10^{-4}$ a/cm², although the rate of the anodic reaction increases approximately a thousand times ^{X/}. This constancy of " i_0 " testifying to a noticeable slowing down of the cathodic reaction with the increase of C_g , convinces us once again that the influence of anions cannot be explained by the changes in the structure of the double layer taking place under the influence of their adsorption and the appearance of a negative ψ - potential (as was done by Franklin ^{8/} for the hydrogen evolution reaction). If these changes in the double

X/ The increase in the concentration of NaCl also led to a shift in the equilibrium potential of the system in the negative direction, according to the equation $\frac{\partial \psi}{\partial \ln C_g} = -0,040$ V.

-7-

layer were the only result of the adsorption of anions, this adsorption would bring about an equal acceleration of both the cathodic and the anodic reaction and consequently to the increase of the exchange current at an invariable equilibrium potential.

At present we can consider as firmly established the existence of a good conformity between the adsorbability of anions on the electrode metal and their ability to form complexes with the corresponding cations. Evidently, because of this a change in the anion content of the solution can lead not only to a change in the energy state of the surface atom but also to a change in the energy state of the metallic ion in the solution. From this point of view the noticeable slowing down of the cathodic reaction with the increase in the concentration of Cl ions can be connected with the fact that the discharge of hydrated ions of Indium takes place with a smaller activation energy than the discharge of complex ions of Indium with Cl .

To understand the mechanism of the anions' action on the kinetics of the anode reaction, the data received in our laboratory during the investigation of the adsorption of Iodine ions on a silver electrode is also of interest. Using radioactive indicators it was established that the degree of surface coverage of the electrode by specifically adsorbed anions, and what is particularly

-8-

important, the strength of the anions' bond with the surface atoms of the metal increase noticeably with the shift of the electrode potential in the positive direction.

The data obtained in studying the dependence of the kinetics of the desorption of Iodine ions on the potential of the preliminary polarisation of the electrode bears out the existence of the effect of the strengthening of the adsorption bonds. Corresponding experiments were carried out in solutions with a very small concentration of KJ, that is in conditions when the potential at which the complete adsorption of iodine ions from the solution can easily be achieved. One and the same degree of surface coverage corresponded to different and more positive potentials than this value.

The results of one of these experiments are given in fig. 5. In this case the kinetics of desorption were determined at one and the same potential equal to $-0.335V$ (in regard to the potential of the reversible hydrogen electrode in the same solution). However, the potentials of preliminary polarisation differed one from the other and equalled $-0.174 V$ (curve 1) and $-0.124 V$ (curve 2). In a $1.0 N H_2SO_4$ solution, containing at the beginning $1.6 \cdot 10^{-9}$ eq./l KJ, one and the same degree of surface coverage $16.9 \cdot 10^{11}$ ions/cm² corresponded to these two potentials. However, in spite of this, the desorption

-9-

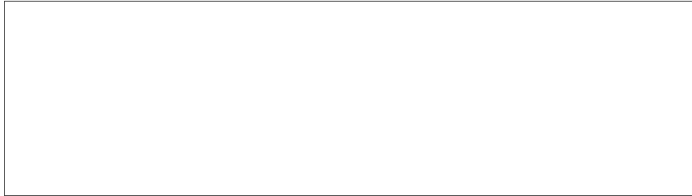
of Iodine ions at a potential equal to -0.335 v proceeded all the slower the more positive the potential of adsorption. Thus, for the above given potentials of preliminary polarisation the subsequent desorption of one and the same quantity of Iodine ions - equal to $4 \cdot 10^{10}$ ions/cm² - took place - other conditions being equal - in 27 and 110 minutes respectively.

On the basis of these results one can also assume that the specific adsorption of anions which begins at much more negative potentials than the potential of the dissolution of the electrode metal should be regarded as the beginning of the formation (with the help of covalent bonds) of the corresponding salt. However, at the early stage of adsorption the strength of this bond differs noticeably from the strength of the bond in the corresponding individual compound. As the potential shifts in the positive direction this difference grows less, and finally disappears altogether. Starting from this potential, the metal begins to go over into the solution in the form of complexes with the anions being adsorbed.

In conclusion it should be noted that the specific adsorption of anions can lead not only to the decrease in the overvoltage of the anodic dissolution reaction, but also in some cases to its noticeable increase, that is to the passivation of the metallic surface. Such

-10-

results were, for instance, obtained in their time by Z.A. Iofa and L.A. Medvedova^{9/}, who showed that the specific adsorption of Iodine ions on iron in acid solutions leads to a noticeable slowing down of the anodic dissolution of this metal. In further investigations it was shown that this slowing down could be observed even in those cases when the quantity of adsorbed Iodine was sufficient for the formation of only a tenth of a part of the monolayer. Unfortunately, these questions go beyond the confines of this paper.



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List of Figures

- Figure 1. Cell used for experiment
- Figure 2. Polarisation curves of Indium Amalgam (0.1M) in a solution of 0.01M $\text{In}(\text{ClO}_4)_3$
 \times - normal polarisation curves,
 \circ - true anodic curve, received radio-chemically
 (\circ - exchange current).
- Figure 3. The dependence of the rate of the true anodic process on the concentration of NaCl at a constant potential ($\varphi = -0,330 \text{ v}$).
- Figure 4. The dependence of the rate of the true anodic process on the concentration of NaBr (triangles) and NaJ (circles) at a constant potential ($\varphi = -0,275 \text{ v}$);
- Figure 5. Partial desorption of Iodine from a silver electrode at a potential $-0,335\text{v}$, after preliminary polarisation of the electrode at potential $= -0,174\text{v}$ (curve 1) and $-0,124 \text{ v}$ (curve 2).

